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CHAPTER XI

CHEMICALS FROM STARCH

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I. INTRODUCTION

Rapidly increasing prices and dwindling supplies of petroleum have inten-
sified interest in natural products as alternative sources of energy and raw mate-
rials for the chemical industry. Starch, a polysaccharide produced in great
abundance in nature, is a prime candidate for use as a raw material because it is
available at a low cost and can be converted readily into a variety of useful
monomeric and polymeric products by chemical and biochemical means.

While there is social and economic controversy over using such natural prod-
ucts as starch for chemicals instead of food, the fact remains that the United
States produces more carbohydrate than is needed for a balanced diet. The six
major cereal grain crops produced in 1977 contained 400 billion pounds of
starch. Most of this starch was fed to animals, despite tests showing better weight
gain with higher protein feeds (*1*). Hence, the nutritional value of grain products
is enhanced by removing part of the starch or by fermenting the starch to alcohol,
leaving a high quality feed known as distillers dried grains. However, these
processes are economically feasible only when a market exists for the starch or
starch-derived products. Hundreds of products from and applications of starch

**The mention of firm names or trade products does not imply that they are endorsed or recom-
mended by the U.S. Department of Agriculture over other firms or similar products not mentioned.*

have been developed over the years. Here we have chosen to emphasize only the more recent and highly promising applications of starch-derived products.

II. Chemicals from Starch via Biosynthesis

Although techniques for fermenting starch to various chemicals have been known for many years, a few processes are discussed here because of current high interest in developing alternative sources of raw materials. The production of some industrial-grade ethanol from natural products is one example of the rising trend toward fermentation biosynthesis (2).

Ethanol is produced in the United States by two major procedures, fermentation and chemical synthesis. Practically all synthetic ethanol is now produced from ethylene. Table I shows the effects of increasing raw material cost from 1973 to 1980 on the cost of producing alcohol from ethylene. These data were based on fixed conversion costs reported in 1976 by Miller (3).

$$CH_2=CH_2 + H_2O \xrightarrow{Catalyst} C_2H_5OH$$
$$\text{ethylene} \qquad\qquad \text{ethanol}$$
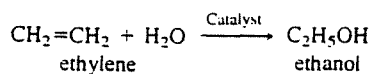
All beverage alcohol is produced in the United States by the fermentation of starch and sugar or from grains and molasses which are high in starch and sugar content, respectively.

Table I

Effect of Ethylene Cost on Ethanol Cost[a]

	Ethylene, cents/pound[b]							
	3.3	7.5	8.8	11.2	12.0	13.0	19.0	23.0
Alcohol	Cost/gallon, cents							
190° Proof								
Ethylene	13.2	30.0	35.2	44.8	48.0	52.0	76.0	92.0
Conversion	26.9	26.9	26.9	26.9	26.9	26.9	26.9	26.9
Total manufacturing cost/gallon (exclusive of profit, packaging, and sales expenses)	40.1	56.0	62.1	71.7	74.9	78.9	102.9	118.9
200° Proof								
Ethylene	13.8	31.3	36.8	46.4	50.1	54.3	79.4	96.1
Conversion	31.3	31.3	31.3	31.3	31.3	31.3	31.3	31.3
Total manufacturing cost/gallon (exclusive of profit, packaging, and sales expenses)	45.1	62.6	68.1	77.7	81.4	85.6	110.7	127.4

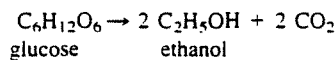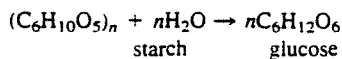[a] Based on conversion costs reported by D. L. Miller in 1976 (3).

[b] Approximate prices of ethylene from 1973 to 1980.

Table II

Effect of Corn Cost on Ethanol Cost

(Basis: 2.7 gal. of 200° proof alcohol/bushel)

Corn price/bushel, dollars	Alcohol cost/gallon, cents		
	Corn	Conversion[a]	Total base cost[b]
2.00	74.0	25.4	99.4
2.25	83.3	25.4	108.7
2.50	92.6	25.4	118.0
3.00	111.0	25.4	136.4
3.50	129.5	25.4	154.9
4.00	148.4	25.4	173.8

[a] By-product grains credited at $100/ton in conversion cost.

[b] These costs do not include profits, packaging, and sales expenses.

$$(C_6H_{10}O_5)_n + nH_2O \rightarrow nC_6H_{12}O_6$$
starch   glucose

$$C_6H_{12}O_6 \rightarrow 2 C_2H_5OH + 2 CO_2$$
glucose   ethanol

One pound of starch should theoretically yield 0.568 lb of ethanol. In actual practice, yields generally are about 90–95% of theory. By allowing a 34 cents per gallon of alcohol of by-product feed credit ($100/ton), D. L. Miller estimated in 1976 that the net cost of converting corn to absolute ethanol was 25.4 cents/gal. The effects of corn prices on the cost of producing fermentation alcohol are shown in Table II (*3, 4*). While this conversion cost has increased since 1976, the by-product feed credit increased so that the cost per gallon reported in Table II remains fairly accurate. The price of fermentation alcohol may be less than these production figures reflect because industrial grain alcohol comes largely from integrated grain milling plants where potable and industrial ethanol are produced along with other corn products.

Interest in fermentation alcohol is further intensified by the prospects of fermenting surplus and low quality grains, sugar, and cellulosic residues into fuel alcohol. Many companies now sell gasohol (90% gasoline, 10% ethanol) and other gasoline–ethanol blends for motor fuel. However, many experts believe that several persistent problems remain to be solved before fermentation alcohol can be expected to replace a significant amount of gasoline fuel. Yet proponents of fuel alcohol maintain that the fermentation of grain to fuel alcohol is already feasible. Regardless of the controversy, considerable state and federal funds have been appropriated for fermentation alcohol research. Undoubtedly, much of these research efforts will be directed toward reducing the energy needed to produce and recover pure ethanol.

Tong (2) reviewed the bioconversion of carbohydrate raw materials into iso-propanol, *n*-butanol, acetone, ethanol, 2,3-butylene glycol, glycerol, and fumaric acid and the subsequent catalytic conversion of butylene glycol to methyl ethyl ketone, fumaric acid to maleic anhydride, and ethanol to butadiene. Of these three catalytic conversions, only the butadiene process from ethanol attained commercial-scale success. Prior to 1950, the bulk of our acetone and *n*-butanol was obtained by the anaerobic fermentation of carbohydrates. Several anaerobic glycerol fermentation processes were developed prior to 1960, but have since been displaced by synthetic routes. From this list of 10 chemicals, Tong reports that, of the total U.S. production in 1976, 5% of the acetone, 10% of the *n*-butanol, 15% of the fumaric acid, and 30% of the ethanol were produced by fermentation.

III. Polyhydroxy Compounds from Starch

Although starch is being considered for the production of alcohol and hydrocarbons as a direct replacement for petroleum, any such conversions are accompanied by drastic mass losses due to the elimination of CO_2 and H_2O. For example, the maximum possible mass yield of ethylene from starch is 52% owing to the loss of oxygen. The only process under consideration for producing ethylene from starch is based on fermenting starch to ethanol followed by dehydration of the ethanol. Based on this process, the loss of both CO_2 and H_2O reduces the maximum mass yield of ethylene from starch to only 34.6%. A more feasible approach to utilizing starch may depend on developing substitutes, rather than direct replacements, for petroleum such that the hydroxyl groups are retained to perform a useful function. Several polyhydroxy compounds have been developed from starch for industrial applications that are less expensive than comparable products made from petroleum.

Glucose, the most common polyhydroxy compound made from starch, is obtained in 90–95% yields by acid or enzymic depolymerization of starch, and because a molecule of water is added, the mass yield of glucose is slightly more than 100%. Glucose can be converted to a variety of cyclic and acyclic polyols, aldehydes, ketones, acids, esters, and ethers, some of which are now used industrially and others which could increase in importance if the price for petroleum and petroleum products continues to rise. Fermentation of simple sugars is now employed as the preferred route to commercial organic acids such as D-gluconic and itaconic. Sorbitol (D-glucitol) is probably the most widely used polyol made from starch or glucose. It is used extensively for making surfactants and emulsifiers, especially for food applications. An estimated 1 to 2 million pounds (900,000 kg) of sorbitol go into making specialty polyethers for urethane foam production. Sorbitol, now priced at 60 cents/lb, is too expensive for many industrial applications.
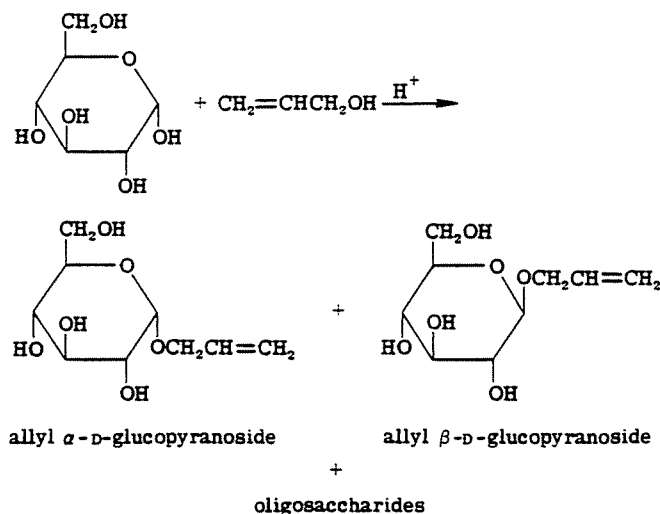
FIG. 1.—Conversion of D-glucose to allyl glucosides.

Methyl α-D-glucopyranoside (methyl glucoside), obtained by the reaction of glucose or starch with methanol, has been produced and evaluated for a number of industrial applications. The most promising of these was for making polyethers for rigid polyurethane foam production (5); but unfavorable economics forced its removal from this market for several years, except for minor specialty uses. In 1982, a corn wet-milling company announced plans to start producing this polyol. Higher alkyl glucosides are made from methyl glucoside by a double alcohol interchange, first with n-butanol then with a C_8 to C_{18} alcohol (6) or by reacting glucose with higher alcohols (7). These higher alkyl glucosides are sold commercially as nonionic detergents, in part because of their high alkali resistance and biodegradability. Methyl glucoside has been extensively evaluated in other surfactant applications (8) as well as in oil-modified urethane coatings (9) and alkyds. Most of the work on methyl glucoside was conducted by J. P. Gibbons and co-workers and published in technical literature by CPC International.

Allyl glucoside was prepared and evaluated in the laboratory as a polyol initiator for making polyethers for flame retardant urethane foam application. One approach involves the stepwise reaction of glucose with allyl alcohol, propylene oxide, and bromine, illustrated in Figures 1 and 2 (10). Alternatively, the halogen was incorporated through free radical addition of CCl_4 and $CBrCl_3$ to the double bond of propoxylated allyl glucoside (11). Similar products were obtained by an alcohol interchange of a commercial-grade methyl glucoside polyether with allyl alcohol followed by halogenation (12). All these polyethers produced good quality, flame-resistant foams.

allyl α-, β-D-glucopyranosides

polyether for urethane foam
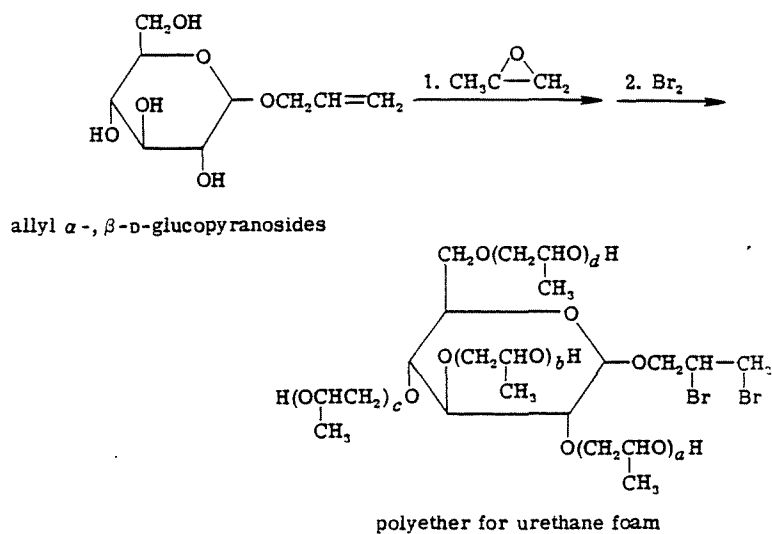
FIG. 2.—Conversion of allyl glucosides to brominated polyethers.

starch unit

2-hydroxethyl α-D-glucopyranoside
("glycol α-D-glucoside")

2-hydroxyethyl β-D-glucopyranoside
("glycol β-D-glucoside")

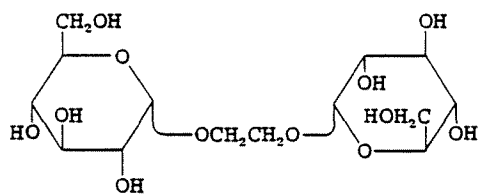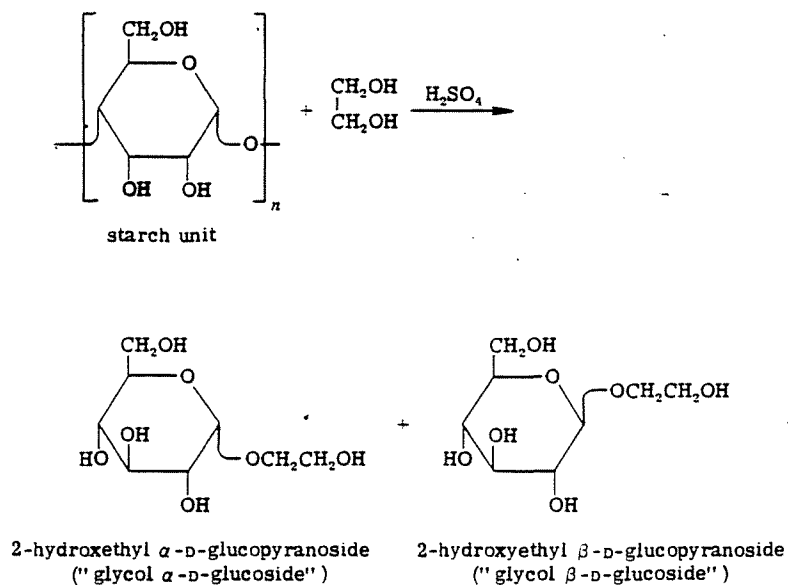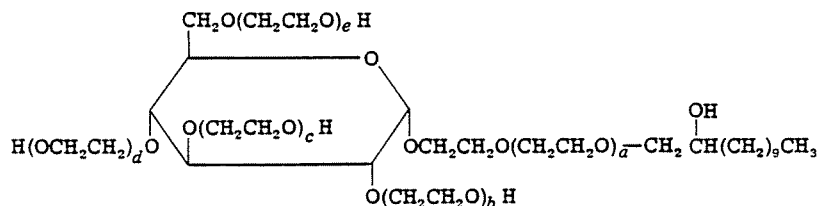ethylene bis(α-D-glucopyranoside)
("glycol diglucoside")

FIG. 3.—Conversion of starch to glycol glucosides.

An experimental polyol, obtained from the reaction of starch with ethylene glycol, may find large-scale application in rigid urethane foams, surfactants, and alkyds. The polyol is made by heating a mixture of 1 mole of starch, 4 moles of glycol, and an acid catalyst at 130° for 45 min. About 0.8 mole of glycol reacts per anhydroglucose unit and a part or all of the remaining is removed by vacuum distillation, depending upon the intended application for the polyol. The product is a mixture of glycol glucoside polyols shown in Figure 3 (*13*). Similar products were obtained by reacting starch with glycerol. In 1969, Ashland Chemical Company, under a USDA contract, estimated a raw material cost of 8.81 cents/lb ($0.194/kg) and an operating cost of 2.03 cents/lb ($0.045/kg) for producing glycol glycosides in a plant designed to make 7 million pounds (3 million kg) per year (*14*). Updating these figures to reflect the 1980 cost of dry starch at 10 cents/lb and ethylene glycol at 34 cents/lb, the approximate raw material cost to produce the glycol glucoside is now 18.5 cents/lb. Conventional polyols such as pentaerythritol and glycerol now sell for 60–65 cents/lb.

The most promising application for these glycol or glycerol glucosides is as polyol initiators for making polyethers for rigid urethane foam production. If glycerol glucosides are used for this application, all the unreacted glycerol need not be removed because it will help lower polyether viscosity and will not greatly affect foam properties. Polyethers are obtained by reacting the crude glucosides with 6 moles of propylene oxide (Fig. 4). Treatment of the polyethers with polyisocyanates in the presence of blowing agent, surfactant, and catalysts produces good quality foams (*15*). The projected 1 billion pounds (450 million kg) per year foam market could utilize about 100 million pounds (45 million kg) of starch. Several companies have evaluated the production of glucoside-based polyethers and one has made large-scale runs.

The glycol and glycerol glucosides were extensively evaluated in the laboratory (*16*) and pilot plant (*17*) as raw materials for biodegradable surfactants. First, the glucosides were reacted with ethylene or propylene oxide or a mixture of the oxides to form alkoxylated glucosides. These products were not fully characterized but apparently the alkoxides were randomly substituted at the hydroxyl sites. The alkoxylated products were then esterified with long-chain fatty acyl groups or etherified with long-chain α-olefin oxides. To illustrate the general class of products, a conceptual structure of an alkyl ether obtained by reacting 1 mole of dodecane 1-oxide with an ethoxylated glycol glucoside is shown. Ob-

$CH_2O(CH_2CH_2O)_e$ H

$H(OCH_2CH_2)_d O$ $O(CH_2CH_2O)_c$ H $OCH_2CH_2O(CH_2CH_2O)_a$—CH_2 $\overset{OH}{\underset{|}{CH}}(CH_2)_9CH_3$
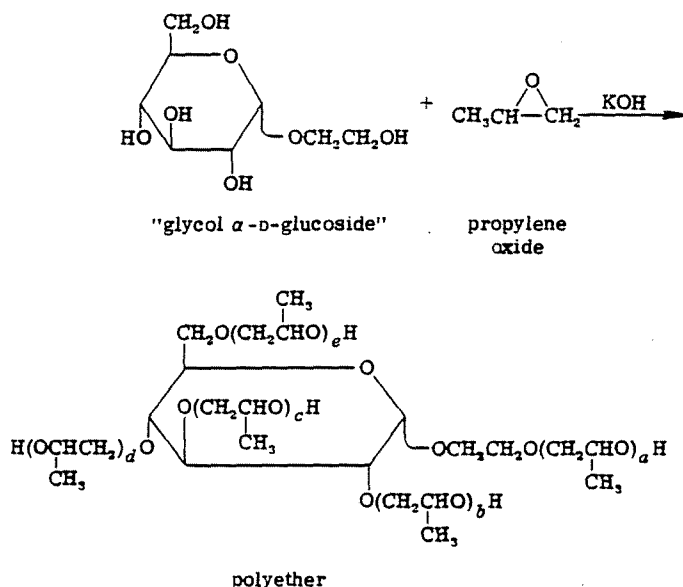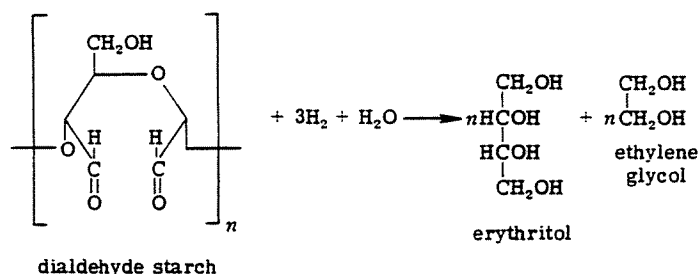
$O(CH_2CH_2O)_b$ H

FIG. 4.—Starch-derived polyethers.

viously, this is only one of five possible isomers since the fatty ether could be attached at any of the hydroxyl sites. The surfactancy and detergency performance of the new products were rated as equivalent to those of ethoxylated octyl phenol. However, they show a significant improvement in biodegradability. Langdon suggested the application of fatty ether glycosides as alkali-stable surfactants (18). Feuge and co-workers (19, 20) have extensively evaluated glycerol glucoside esters in emulsifier applications. Others have made and evaluated food emulsifiers from the glycerol glucosides (21).

Glycol glucosides were studied for use in both conventional and urethane alkyds (14). These alkyds were evaluated in both clear and pigmented films and were found to have superior drying and hardness, and equivalent flexibility, but slightly inferior gloss and yellowing characteristics when compared with industrial controls based on pentaerythritol–glycerol polyols. Preferably, the alcoholysis or esterification reactions were conducted with a mixture of up to 55% glycol glucoside and at least 45% glycerol, which suggests that glycerol glucosides made without removing all excess glycerol would be the more economically feasible route to making these alkyds.

Other polyols have been made from starch, including erythritol and ethylene glycol which were prepared in 90% of theory by reductive hydrolysis of dialdehyde starch (22). This process is not expected to become industrially feasible unless dialdehyde starch is made available at the lowest possible cost. Numerous studies have been conducted on the hydrogenolysis of saccharidic materials, such

as dextrin, starch, and glucose; a variety of polyols are produced (23). The low cost of starch and increasing costs of petroleum-based polyols suggest that additional research could lead to economically feasible routes for enzymically or chemically depolymerizing starch into low-molecular-weight polyols for such applications as antifreeze and synthetic fabric production.

$$\text{dialdehyde starch} + 3H_2 + H_2O \longrightarrow n\,\text{erythritol} + n\,\text{ethylene glycol}$$

$$
\underset{\text{dialdehyde starch}}{
\left[
\begin{array}{c}
CH_2OH \\
\end{array}
\right]_n
}
+ 3H_2 + H_2O \longrightarrow
n\underset{\text{erythritol}}{
\begin{array}{c}
CH_2OH \\
HCOH \\
HCOH \\
CH_2OH
\end{array}
}
+ n\underset{\text{ethylene glycol}}{
\begin{array}{c}
CH_2OH \\
CH_2OH
\end{array}
}
$$

IV. Starch in Plastics

A large portion of the chemicals produced from petroleum is utilized to manufacture the nearly 40 billion pounds (18 billion kg) of synthetic polymers now used annually in the United States. Plastics, which now account for about 75% of the total synthetic polymer production, will double in usage volume during the next decade if raw materials are available. In recognition of this growth potential and the uncertainties in availability of sufficient petroleum feed stocks, interest has increased in the use of natural polymers as extenders for plastics and as total replacements for certain types of plastics. Not only is it the renewable aspect of raw materials such as starch that has piqued the interest of industry, but also the potential of such natural polymers to impart biodegradability to fabricated materials. Because of concern over buildup in the environment of discarded plastic goods due to their resistance to microorganisms, the plastics industry is giving considerable attention to this area. If plastics can be made readily biodegradable, new markets for such materials would materialize, and the growth for plastics would likely exceed even the most liberal estimates.

Starch was evaluated as an inert filler in poly(vinyl chloride) (PVC) plastics, as a reactive filler in rigid urethane foams, and as a component in poly(vinyl alcohol) and ethylene–acrylic acid copolymer films. Three techniques were investigated for incorporating large amounts of starch as a filler in PVC plastics (24). In one, a starch derivative was coprecipitated with a PVC latex and the coprecipitate was filtered off, dried, hammer-milled to a fine powder, blended with dioctyl phthalate (DOP), and molded in an aluminum cavity. In a second, starch was gelatinized and mixed with PVC latex, and water was removed from the mixture in an oven. The dry product was milled, mixed with DOP, and molded as before. The third technique involved dry blending starch, PVC, and

Table III

Properties of Plastics Made with Starch and 25 Parts of DOP
per 100 Parts of PVC[a]

Starch, %	Tensile strength, psi	Elongation, %	Specific gravity	Fungi resistance[b]	Clarity[c]
Coprecipitate: Starch Xanthate–PVC (Geon 151)
0	2,560	133	1.27	0	12
12.3	2,720	66	1.23	1	12
32.9	2,240	8	1.36	4	16
51.0	1,920	5	1.35	3	20
Coconcentrate: Starch–PVC (Geon 151)
0	3,650	140	—	0	13
12.9	3,220	44	1.24	1	16
34.0	3,360	13	1.31	4	15
Dry Mix: Starch–PVC (Geon 126)
0	2,600	150	1.25	0	6
13.4	2,170	110	1.27	1	43
38.2	1,370	31	1.30	4	85
Dry Mix: Starch–PVC (Geon 102)
0	3,600	140	—	0	—
30	2,930	104	—	—	70
40	3,040	35	—	—	78

[a] DOP = dioctyl phthalate; PVC = poly(vinyl chloride).

[b] ASTM D-1924-70, fungus growth; 0 = none; 1 = 10%; 2 = 10–30%; 3 = 30–60%; 4 = 60–100%.

[c] Relative values: 0 is completely clear and 100 is opaque.

DOP on a rubber mill and then molding. Tensile strength remained good even with as much as 50% starch in the plastic (Table III). Clarity of the plastics also was good except for those made by dry blending, but elongation decreased rapidly as the starch level increased.

The three formulations were also blended on a rubber mill until films could be removed from the rolls. Properties of the film were measured and their longevity in Weather-Ometer and outdoor exposure tests was evaluated (Table IV). By varying the composition, films were obtained that lasted from 40 to 900 h in the Weather-Ometer and from 30 to more than 120 days in the soil. All samples tested under standard conditions with common soil microorganisms showed mold growth, with the greatest amount of growth recorded for samples containing the highest amount of starch.

One area of application for biodegradable plastic film is agricultural mulch. An estimated 60 million pounds (27 million kg) of plastic mulch is used in the

United States to improve the yield and quality of vegetable and fruit crops such as tomatoes, peppers, melons, and sweet corn. Mulch helps to control soil moisture and temperature, reduce nutrient leaching, prevent weed growth, and increase crop yields by 50–350%. Polyethylene film, commonly used for mulch, does not degrade between growing seasons and must be removed from the field and buried or burned at an estimated cost of $100 per acre ($250/hectare). Considerable interest has been expressed in using a degradable mulch to obviate the need for removal and disposal (25).

Griffin reported that starch can be incorporated into low-density polyethylene (LDPE) film to impart biodegradable properties (26). Based on this work, Color-oll Ltd., England, is now producing a polyethylene bag that contains 7–10% starch and is reportedly biodegradable.

Starch–poly(vinyl alcohol) (PVA) films may have application as a degradable agricultural mulch. In preliminary studies, a composition containing 60–65% starch, 16% PVA, 16–22% glycerol, 1–3% formaldehyde, and 2% ammonium chloride was combined with water to give 13% solids and heated at 95° for 1 h. The hot mixture was then cast and dried at 130° to a clear film. Films, on removal from the hot surface, were passed through a solution of PVC or Saran to coat the film with a water-repellent coating. Uncoated films are insoluble in water, but their wet strength is low. Coated films retain good strength even after water soaking. Weather-Ometer tests suggest that film with 15–20% coating might last 3–4 months in outdoor exposure (27).

Since 1977, one company has been using the starch–PVA technology to produce a water-soluble laundry bag for use by hospitals in which to keep soiled or contaminated clothing prior to washing. The bags and their contents are placed directly into washing machines, where the bag dissolves. In order to provide enhanced solubility, a slightly derivatized starch is used for this application.

Table IV

Properties of Starch–PVC–DOP Films

Starch		PVC resin		DOP, PHR[a]	Tensile strength, psi	Outdoor exposure,[b] days	Weather-Ometer,[b] h
Type	%	Type	%				
Whole	25.1	Geon 126	57.5	25	1,720	120	458
Xanthate	40.5	Geon 151	39.7	50	1,860	>150	120
Gelatinized	44.0	Opalon[c]	37.2	50	740	52	170
Gelatinized	36.4	Geon 151	36.4	75	420	66	—

[a] Parts of DOP per 100 parts of PVC.

[b] Films showed major deterioration after given time.

[c] Monsanto Company.

Such water-soluble bags are also being suggested for packaging agricultural chemical pesticides to improve safety during handling.

$$-CH_2-CH_2-CH_2-\underset{\underset{COOH}{|}}{CH}-CH_2-CH_2-CH_2-CH_2-CH_2-\underset{\underset{COOH}{|}}{CH}-$$
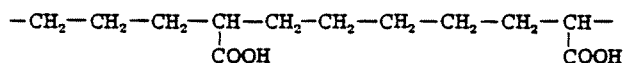
EAA

Films that have potential application in biodegradable mulch, packaging, and other products were obtained from various combinations of starch and ethylene–acrylic acid copolymer (EAA). Three forms of EAA obtained from Union Carbide Corp. were evaluated: PCX-300, dry pellets; PCX-140, a mechanically produced latex containing 40% EAA; and PCX-100, a 25% ammonium solution of EAA. The EAA has a carbon backbone with occasional pendant carboxyl groups that can react with ammonium hydroxide to solubilize the resin. The EAA evaluated contained about 20% reacted acrylic acid. Films were prepared by casting heated aqueous dispersions of starch and the copolymer followed by oven drying or by fluxing dry mixtures of starch and EAA on a rubber mill. Properties of these films are listed in Table V. The starch–EAA system can also be ex-

Table V

Properties of Starch–Ethylene Acrylic Acid Copolymer Films from Aqueous Dispersions and Dry Mixing on a Rubber Mill

Composition, %			Tensile strength, psi	Elongation, %	Folding endurance, no. double folds	Burst factor	Fungi[a] resistance
Starch	EAA	Stearic acid					
Starch and PCX-100							
0	100	0	3288	295	No break	21.8	0
20	76	4	2483	116	2972	20.7	2
40	56	4	2528	44	531	21.7	4
60	37	3	3186	21	349	20.6	4
80	19	1	5345	10	61	15.0	4
Starch and PCX-140							
0	100	0	3336	349	—	—	0
20	80	0	3898	226	—	—	4
40	60	0	4077	87	—	—	4
60	40	0	4993	44	—	—	4
Dry Mixtures of Starch and PCX-300							
0	100	0	6699	48	—	—	0
20	80	0	4519	48	—	—'	0–1
40	60	0	1897	53	—	—	4
60	40	0	2685	21	—	—	4

[a] ASTM D 1924-63; mold coverage: 0 = none; 2 = 10–30%; 3 = 30–60%; 4 = 60–100%.

truded. Duplicate samples of the cast films containing 30, 40, 50, 70, and 90% starch were exposed to outdoor soil contact, with the ends buried in soil, to observe their resistance to sunshine, rain, and soil microorganisms. Films with more than 40% starch deteriorated within 7 days while those containing 30 and 40% starch remained flexible and provided mulch protection for at least 30 days. When the films containing up to 50% starch were formulated with 2% paraformaldehyde, they provided good soil protection for at least 70 days. These preliminary soil exposure tests demonstrate that starch–EAA films are biodegradable. Furthermore, some control in the rate of biodegradation can be built into the films by varying the amount of starch used and by adding a fungicide such as paraformaldehyde. Other tests revealed that the starch–EAA films have sufficient strength, flexibility, water resistance, and heat sealability for a variety of mulch and packaging applications (28).

In a subsequent study, films were prepared and evaluated from various combinations of starch and pelletized EAA, using the less expensive extrusion blowing technique (29). Extrusion blowing is a common, economical method for producing film in which a tubular extrudate is expanded and shaped by internal air pressure to form a bubble several times the size of the die opening. The process also allowed the incorporation of LDPE as a partial replacement of the EAA, which further reduced the film cost and in some instances improved properties. Properties of the films are shown in Table VI.

Not only can starch be mixed with synthetic polymers and exhibit utility as a filler, extender, or reinforcing agent, it can also become an integral part of such polymers through chemical bonds. Urethane is an example of a system where starch has been chemically bonded to a resin. To produce relatively low-cost, rigid urethane plastics that might have application in solvent-resistant floor tile, a system was developed based on 10–60% starch, castor oil, the reactive products of castor oil and starch-derived glycol glycosides, and polymeric diisocyanates (30). The addition of starch to the isocyanate resins substantially reduced chemical costs and improved solvent resistance and strength properties. Evidence showed that the starch chemically combined with the resin molecules.

The degree of reactivity between starch and isocyanates can be greatly enhanced by modifying starch with non-polar groups, such as fatty acid esters, before the isocyanate reaction (31). Maximum reactivity of the modified starches was achieved when the degree of substitution was about 0.7.

Elastomers have been prepared with starch as a filler and crosslinking agent for diisocyanate-modified polyesters (32). Dosmann and Steel (33) reported that starch can be incorporated into urethane systems to yield shock-resistant foams. Bennett and co-workers (34) found that up to 40% starch or dextrin can be incorporated into rigid urethane foam and that such foams are more flame resistant and more readily attacked by microorganisms.

An alternative approach to making plastics from starch may depend upon the

Table VI

Effect on Film Properties of Starch and LDPE Levels

Run no.	Formulation, %[a,b] Starch	EAA	LDPE	Tensile strength, psi	Elongation, %	Ammonia[c]	MIT fold, no. folds	Burst factor	Weather-Ometer, h	Fungi susceptibility, weeks[d] 1	2	3	4
1	10	90	0	3470	260	4.9	—	—	402	0	0	0	0
2	20	80	0	4140	120	4.3	—	—	212	0	0	0	0
3	30	70	0	3225	150	3.8	—	—	168	0	0	0	0
4	40	60	0	3870	92	3.3	—	—	90	1	1	1	1
5	50	50	0	3940	61	2.7	—	—	90	1	2	3	3
6	40	50	10	3570	80	3.6	3800	24	111	2	3	4	4
7	40	40	20	3477	66	2.2	7000	24	134	1	2	3	4
8	40	30	30	3150	85	1.7	2700	21	151	1	2	3	4
9	40	20	40	2920	34	2.8	4800	19	199	—	—	—	4
10	40	10	50	1840	10	2.8	470	9	559	—	—	—	4
11[e]	30	32.5	32.5	2000	62	1.6	—	—	710	—	—	—	—

[a] Based on combintion dry weight of starch, EAA, and PE, exclusive of water and NH_3.

[b] Formulations of examples 4, 6, 9, and 11 additionally contained about 1% antioxidant ("Irganox 1035," Ciba Geigy Corp.)

[c] Parts of ammonia per 100 parts of formulation dry weight.

[d] ASTM D 1924-70, fungus growth, 0 = none, 1 = 10%, 2 = 10-30%, 3 = 30-60%, 4 = 60-100%.

[e] Formulation contained 5% carbon black (Industrial Reference Black, No. 3).

use of microbial polysaccharides. One such example includes pullulan, a linear chain of maltotriose units, obtained by the action of a yeast-like fungus on starch. In a review of this subject, Shipman and Fan (35) report that pullulan-derived plastics resemble styrene in gloss, hardness, and transparency, but are much more elastic.

V. STARCH GRAFT COPOLYMERS

1. Starch Graft Copolymers in Plastics

Another approach to chemically bonded natural polymer–synthetic polymer compositions is through graft polymerization. This technique has received considerable attention of scientists at the Northern Regional Research Center, especially for those systems where the natural polymer is starch. Basically, the procedure used for synthesizing starch graft polymers is to initiate a free radical on the starch backbone and then allow the radical to react with polymerizable vinyl or acrylic monomers. A number of free-radical initiating methods have been used to prepare graft copolymers and these may be divided into two broad categories: initiation chemically and by irradiation. The choice depends in part on the particular monomer or combination of monomers to be polymerized. A conceptual structure of a starch graft polymer is shown in Figure 5. Both chemical and irradiation initiating systems have been employed to graft polymerize onto starch a wide variety of monomers, both alone and in selected combinations. Fanta and Bagley (36) recently reviewed these systems.

For plastic or elastomeric copolymer compositions which can be extruded or milled, monomers such as styrene, isoprene, acrylonitrile, and various alkyl acrylates and methacrylates were employed.

Starch-graft-polystyrene, -poly(methyl methacrylate), -poly(methyl acrylate), and -poly(methyl acrylate-co-butyl acrylate) polymers have been prepared with approximately 50% add-on and evaluated for extrusion processing characteristics (37). A 20:80 (by weight) mixture of starch-graft-polystyrene and commercial polystyrene produced an extrudate which was filled with particles of unfluxed graft copolymer after two passes through the extruder at 150°. Addition of glycerol to the mixture as a plasticizer for starch did not greatly improve extrudate properties. However, when the graft copolymer was extruded at 175° in the absence of additives, a continuous, well-formed extrudate was produced. Tensile strengths for specimens milled from the extrudate were in the range 7500–9100 psi (527–640 kg/cm²) (Table VII).

Two starch-graft-poly(methyl acrylate) products, one prepared from granular starch and the other from gelatinized starch, were extrusion processed under various conditions. The graft copolymer prepared from granular starch was extruded (three passes) through a 1 × 0.020-in. (25 × 0.5-mm) slit die at 160° and
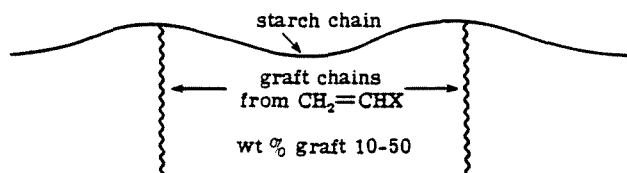
Fig. 5.—Conceptual structure of starch graft polymers. When X = —CO_2H, —$CONH_2$, —$CO_2(CH_2)_n^+$—NR_3Cl^- products are water soluble and useful as thickeners, absorbents, sizes, adhesives, and flocculants. When X = —CN, —CO_2R, products are water insoluble and potentially useful as resins and plastics.

a barrel temperature of 150°. The extruded ribbon was smooth and translucent and exhibited good tensile strength (3000 psi, 211 kg/cm²) and little die swell. Lower extrusion temperatures produced an extrudate which contained unfluxed polymer, and only a crumbly mass was obtained at 125°.

The graft copolymer prepared from gelatinized starch was extruded (one pass) at 125° with a die temperature of 140° to give an extrudate which resembled that obtained from granular starch, but which was less brittle. When extruder and die temperatures were lowered to 100°, a continuous plastic was still produced, although there was an appreciable amount of unfluxed polymer. Tensile strength of the higher temperature extrudate was on the order of 2500 psi (176 kg/cm²) and die swell was minimal. Prolonged soaking of the extrudate in water at room temperature produced a material that was white, soft, and pliable and that showed appreciable increases in both weight and thickness (Table VIII). The specimen surface, however, was not sticky, and the plastic remained continuous and showed no tendency to disintegrate. To estimate biodegradability, a portion of the extrudate was incubated for 5 days at 25° with three different cultures in a nutrient solution as suggested by ASTM DI924-70. *Aspergillus niger* and *Trichoderma viride* gave good growth and sporulation. *Penicillium funiculosum* produced little sporulation but gave good growth.

Ceric ion-initiated graft polymerization of acrylonitrile, methyl acrylate, and chloroprene onto gelatinized cationic starch yielded copolymers with up to 60% polyvinyl side chains (*38, 39*). When starch-graft reaction mixtures of any of the copolymers were sonified at 20 kHz for 1–3 min, latexes that dried at room temperature or 70° to clear adhesive films resulted. Viscosity of the sonified dispersions of about 8% concentration was in the range 10–40 cP. Molecular weights of synthetic side chains were influenced by the type of cationic charge on the starch and on the type of stirring action employed during the polymerizations (Table IX). Number-average molecular weights in the range of 100,000 to 1,000,000 were readily obtainable. This work was recently extended to the preparation of starch-graft-poly(styrene-*co*-acrylonitrile) latexes (*40*). Interest in the preparation of latexes with higher solids content at low viscosities and in the evaluation of the latexes in various end-use applications continues.

Table VII

Polysaccharide Graft Copolymers

Monomer, g	Polysaccharide, g	Water, mL	Initiator	% Add-on[a] Weight gain	% Add-on[a] Weight loss	Graft MW	UTS,[b] psi
Styrene (40)	Granular starch (40)	10	⁶⁰Co, 1.0 mrad	48[c]	—	—	7,500–9,100
Styrene (40)	Granular starch (40)	10	⁶⁰Co, 1.0 mrad	40	41	710,000	—
Methyl methacrylate (160)	Gelatinized starch (100)	2,500	Ce^{4+}	47	50	1,360,000	—
Methyl acrylate (300)	Granular starch (250)	2,000	Ce^{4+}	39	41	845,000	3,000
Methyl acrylate (120)	Gelatinized starch (100)	2,500	Ce^{4+}	44	42	861,000	2,500
Methyl acrylate (63.7)	Cellulose (53.2)	2,000	Ce^{4+}	49	—	—	—
Methyl acrylate (75) and butyl acrylate (75)	Gelatinized starch (100)	2,500	Ce^{4+}	53	—	—	—

[a] Weight gain: % add-on determined by gain in weight of starch after graft polymerization. Weight loss: % add-on determined by loss in weight of graft copolymer after depolymerization and removal of starch.

[b] UTS: Ultimate tensile strength of the extruded plastic.

[c] Crude graft copolymer; homopolymer not extracted.

Table VIII

Effect of Water
on Starch-Graft-Poly(methyl acrylate) Extrudate[a]

Immersion	% Increase		
time, h	In weight	In thickness	In width
0	—	—	—
22.5	54	41	12.5
476.0	53	41	12.5

[a] 1 × 0.022 in. extrudate from polymer 5, Table VI. Extruded at 125° with die temperature of 140°. Soaked in water at room temperature.

Young and co-workers (41) report the development and evaluation of a modified starch containing acrylamidomethyl groups, starch-$OCH_2NHCOCH=CH_2$, capable of polymerization to produce cross-linking within the starch or copolymerization with water-soluble acrylate monomers to yield an acrylic network. Among a variety of potential applications for the starch product, plastics have been formulated for ultraviolet and thermal cure.

2. Starch Graft Copolymers as Water Absorbers

A wide variety of other monomers have been graft polymerized onto granular and gelatinized starch, and several of the graft polymers show promise as thick-

Table IX

Influence of Cationic Functionality (CF) on Starch on Number-Average
Molecular Weight ($\overline{M}_n$) of Grafted Polyacrylonitrile [Poly(AN)]

CF[a]	N, %	Agitator	AGU/Ce(IV)	Starch graft product, N, %	Poly(AN), $\overline{M}_n$
TA	0.42	ST[b]	40	12.25	1,094,000
TA	0.42	SH[c]	40	13.50	506,000
QA	0.39	ST	45	13.07	232,000
QA	0.39	SH	45	12.81	178,000

[a] Cationic starch (24 g), gelatinized in 600 mL of water by heating under nitrogen for 30 min, was cooled to 25°, and reacted with AN and cerium(IV) reagent. The AN:AGU molar ratio was 3.1 and the reaction time, 3 h. TA = tertiary amine; QA = quaternary amine.

[b] Reaction was conducted in a round-bottomed flask using a rotating blade stirrer at 240 rpm.

[c] Reaction was conducted in a stoppered Erlenmeyer flask clamped to a Burrell wrist-action shaker.

starch free radical $+$ $CH_2{=}CHCN$ $\longrightarrow$ starch

$$\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad +\!\!\!\!-\!\!CH_2{-}\underset{\underset{CN}{\displaystyle|}}{CH}\!\!+_x$$

starch-polyacrylonitrile
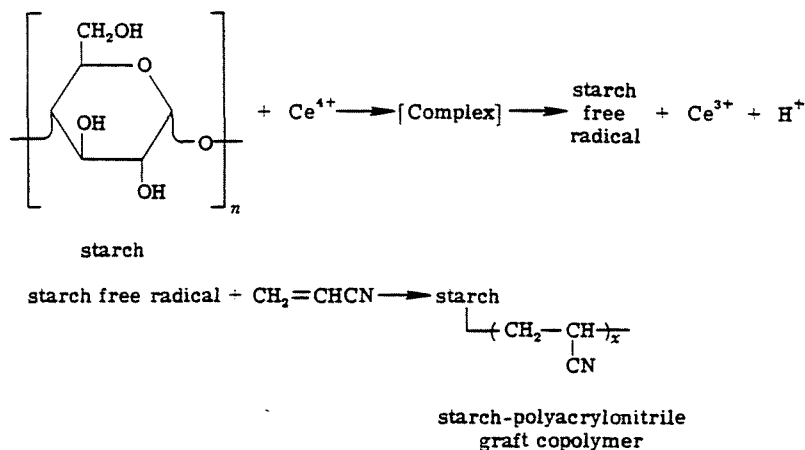**graft copolymer**

FIG. 6.—Preparation of starch–polyacrylonitrile graft copolymer.

eners for aqueous systems, flocculants, clarification aids for wastewaters, retention aids in papermaking, and many other uses. The polymer that has received the most attention and is now being marketed by four U.S. companies is made by graft polymerizing acrylonitrile onto gelatinized starch and subjecting the resulting starch-graft-polyacrylonitrile copolymer to alkaline saponification to convert the nitrile groups to a mixture of carbamoyl and alkali metal carboxylate groups (Fig. 6). Removing the water from this polymer provides a solid which absorbs many hundreds of times its weight of water but which does not dissolve (Fig. 7). Because of its ability to rapidly absorb such large amounts of water, it has been named Super Slurper. As of this writing the U.S. Department of Agriculture has granted more than 50 non-exclusive licenses to parties interested in practicing the technology covered in the four patents issued in 1976 on work with this starch graft polymer (42).

Aqueous dispersions of saponified gelatinized starch-graft-polyacrylonitrile can be cast to yield films on drying. These films are brittle but can be plasticized to improve flexibility. Flexible films can be obtained on casting aqueous dispersions of the graft copolymer containing an anionic or nonionic latex (43). The films will absorb several hundred times their weight of distilled water to give
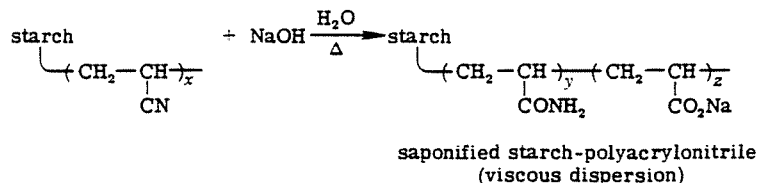
starch $\quad\quad\quad + $ NaOH $\xrightarrow[\Delta]{H_2O}$ starch

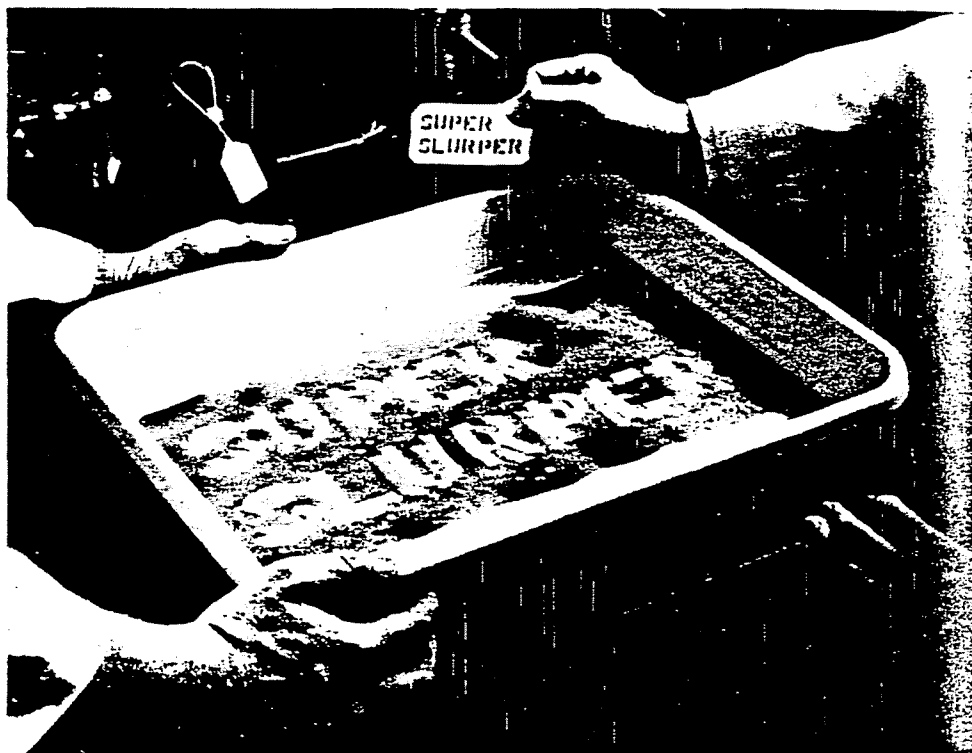FIG. 7.—Saponification of starch–polyacrylonitrile graft copolymer.

FIG. 8.—Absorbency of Super Slurper in film form.

clear sheets of gel, which remain strong enough to maintain their integrity. Also, despite a thirtyfold increase in surface area upon imbibing water, the exact shape of the dry film is retained (44) (Fig. 8). Reducing the pH of the water to about 3 causes the gel sheet to retract to its original size, and raising the pH back to about 7 or higher causes the film to return to a highly swollen gel sheet.

Other forms of the absorbent polymer are obtained by alternative methods of drying. Alcohol precipitation yields a granular or powdery product, whereas drum drying affords flakes and freeze-drying gives spongy mats. Selected end-use applications may dictate the form of the product most desirable.

For application as an additive to absorbent soft goods, such as disposable diapers, incontinent pads, bandages, hospital bed pads, and catamenials, interest has been expressed in the powder, film, and mat forms and the first two forms are being used commercially in incontinent pads and hospital bed pads. The ability of the absorbent polymer to retain most of its absorbed fluid under pressure is a desirable property for such applications (45) (Table X). Under a pressure of 45 × g, a Super Slurper product which had absorbed 648 times its weight of water still retained 409 times its weight. Cellulose fibers, on the other hand

initially absorbed 40 times their weight of water and retained only 2.1 times their weight under this pressure.

Partial hydration of the starch graft copolymer provides a hydrogel especially effective in treating skin wounds of animals (46). The hydrogel absorbs large quantities of fluids secreted by the wounds, provides relief from pain, and prevents drying of subcutaneous tissue. Clinical trials with the hydrogel conducted with human patients suffering from decubitus ulcers or stasis ulcers gave excellent results (47). All skin ulcers responded favorably to the treatment, and the wounds either healed completely or developed a cleaner bed of granulation tissue. In every case, the hydrogel dressing resulted in less eschar formation, fewer infections, and less odor than when ulcers were treated by other methods.

Agricultural applications, such as for seed and root coating and as an additive to fast-draining soils to retain water, appear most promising for Super Slurper. Large-scale field trials with corn, soybean, and cotton seed coated with the polymer have shown increased germination and seedling emergence, and in most trials, increased yield. The dipping of bare-rooted seedlings in hydrated polymer before transplanting overcomes transplant shock and greatly increases survival. For such applications, the powder or granular form is being used.

Grafting of acrylonitrile onto granular (rather than gelatinized) starch followed by saponification in an alcoholic medium also produces an absorbent product (48). The polymer produced by this route is under commercial development by Grain Processing Corporation.

Salts of the hydrolyzed starch-graft-polyacrylonitrile copolymer have been evaluated as thickening agents for aqueous systems (49). These studies showed that the saponified product was readily recoverable from the saponification mass by lowering the pH to about 3. At this pH. the carboxylate groups are converted to the acid form which causes the polymer to precipitate for easy recovery by filtration or centrifugation. Resuspension of the dry product in water and adjustment of the pH to about 7 produces a low solids viscous dispersion with visible,

Table X

Absorbency of Hydrolyzed Starch-Graft-Polyacrylonitrile (H-SPAN) vs. Cellulose Fibers

Absorbent	Fluid	g Fluid/g absorbent		
		Free draining	45 × g	180 × g
Cellulose fibers	Water	40	2.1	1.05
	Simulated urine	32	1.8	1.0
H-SPAN (insoluble) air dried	Water	648	409	—
	Simulated urine	54	40	37
H-SPAN (insoluble) drum dried	Water	896	—	—
	Simulated urine	60	—	—

highly swollen, gel particles. Taylor and Bagley (50) confirmed the presence of a substantial gel fraction by isoionic dilution experiments, which failed to yield linear reduced viscosity-concentration plots, and also by an ultracentrifugation study, which showed that water dispersions of the polymer contained only about 20% solubles. They propose that the tremendous thickening action of the polymer in water is due to the nearly complete absorption of solvent by gel to give a system consisting of highly swollen, deformable gel particles closely packed and in intimate contact. Neither the minor amounts of graft copolymer in solution nor the size of the gel particles exerts a large influence on rheological properties. Under high-dilution or high-ionic strength conditions, solvent is in excess; the gel particles are no longer tightly packed, and the viscosity therefore drops sharply.

VI. Starch Xanthide

1. Starch Xanthide in Rubber

.The use of starch as a replacement for carbon black has been studied in detail at the Northern Regional Research Center. Cross-linked starch xanthate was incorporated into rubber to provide reinforcement to the same extent as medium grades of carbon black (51) (Table XI). Domestic use of carbon black in rubber is about 3 billion pounds, virtually all of which is derived from petroleum. By modification of the process for incorporating the starch derivative into rubber, a

Table XI

Comparative Vulcanizate Properties
of Extrusion Processed Starch-SBR and Black Reinforced SBR Rubbers

Vulcanizate[a]	Hardness shore A	Tensile strength, psi	Elongation, %
50 phr starch xanthide-SBR 1,500	70	2,730	310
50.4 phr FEF black-SBR 1,500	63	2,900	360
50.4 phr SRF black-SBR 1,500	58	2,380	480
50.4 phr FT black-SBR 1,500	51	1,880	690
50.4 phr MT black-SBR 1,500	51	1,340	510
Premium grade passenger tread	58	2,990	600
100 level passenger tread	56	2,550	620
First line competitive tread	58	2,290	590

[a] Blacks used were fine extrusion furnace black (FEF), semi-reinforcing black (SRF), fine thermal black (FT), and medium thermal black (MT).

Table XII

Formulation Designation

Compound type[a]	Form of polymer base		
	Slab	Powdered rubber with 5 or 6 phr SX[b]	Powdered rubber with 20 phr SX
I. Shoe heel	I.S	I.5	I.20
II. Shoe sole	II.S	II.5	II.20
III. Tire tread	III.S	III.5	III.20
IV. Mechanical compound (mixed polymer base)	IV.S	IV.5	IV.20
V. Mechanical compound (SBR polymer base)	V.S	V.5	V.20
VI. White NBR compound	VI.S	VI.5	VI.20

[a] Roman numerals correspond to the formula type and S, 5, and 20 correspond to the nature of the raw polymer used. S corresponds to slab rubber; 5, to powdered rubber with 5 or 6 phr SX; and 20, to powdered rubber with 20 phr SX.

[b] SX = starch xanthide.

simple and economically feasible process was developed for making powdered rubber, a long-sought goal of the rubber industry. A crosslinked starch xanthate–rubber coprecipitate containing 3–5% starch and 95–97% rubber can be readily blended with various rubber additives (Table XII) and injection molded to finished rubber goods with good properties (*52, 53*) (Table XIII). Preliminary calculations, based on an estimated 50% market penetration, suggest that the United States could save 2.5 billion kilowatt hours of electricity annually by using the new process (Fig. 9).

Table XIII

Tensile Properties of Milled and Compression-Molded Shoe Sole and Tire Tread Compounds

Compound No.[a]	At break			Modulus	
	Tensile strength, psi	Elongation, %	10 min set, %	100%	300%
II.S	1,500	420	35	140	600
II.5	1,500	340	20	360	1,200
II.20	1,490	340	30	320	1,150
III.S	2,200	420	25	240	1,560
III.5	2,400	350	30	440	2,000
III.20	2,880	470	35	400	1,700

[a] Designations refer to products listed in Table XI.

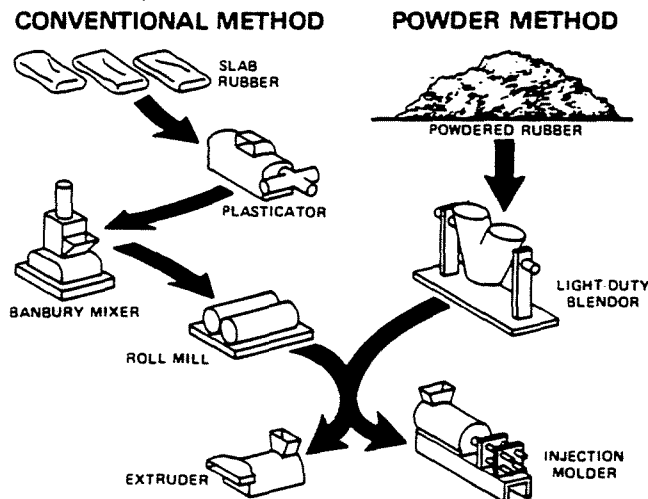**CONVENTIONAL METHOD**   **POWDER METHOD**

FIG. 9.—Comparison of processing rubber by conventional vs. powder methods.

2. Starch Xanthide Encapsulation

A new technology has been developed for encapsulating a broad range of chemical pesticides within a starch matrix to improve safety in handling and reduce losses of the pesticide in the environment due to volatility, leaching, and decomposition by light (*54, 55*). The procedure, based on starch xanthate, consists of dispersing the pesticide in an aqueous starch xanthate solution and subsequently cross-linking the starch xanthate either oxidatively, or with multi-valent metal ions, or with difunctional reagents such as epichlorohydrin (Fig. 10). Cereal flours, which contain about 10% protein along with starch, also can be xanthated and used as an encapsulating matrix. Upon crosslinking, which is effected within a few seconds under ambient conditions, the entire mass becomes gel-like and, on continued mixing for an additional few seconds, becomes a particulate solid which can be dried to low moisture content with only minimal or no loss of the entrapped chemical. That only a single phase is produced on crosslinking with no supernatant is important in assuring essentially complete entrapment of both water-soluble and water-insoluble pesticidal chemicals.

Both solid and liquid pesticides have been encapsulated by this procedure. Where the pesticide is a liquid or finely divided solid, it is added as such to the aqueous solution. For pesticides provided as granular solids, they are first dissolved in any appropriate solvent and then added to the solution. Formulations were made containing up to 55% by weight of liquid pesticides and even higher amounts of solid ones.

Starch-encapsulated formulations have excellent shelf life: no loss of pesticide was recorded on storage in closed containers for up to a year. During storage in

starch + NaOH + CS_2

$\downarrow$

$$\text{starch}-\overset{\overset{\textstyle S}{\textstyle \|}}{\text{OC}}\text{SNa}$$

starch xanthate

HNO_2 / \ Zn^{2+}

$$\text{starch}-\overset{\overset{\textstyle S}{\textstyle \|}}{\text{OC}}\text{S}-\overset{\overset{\textstyle S}{\textstyle \|}}{\text{SC}}\text{O}-\text{starch} \qquad \text{starch}-\overset{\overset{\textstyle S}{\textstyle \|}}{\text{OC}}\text{S}-\text{Zn}-\overset{\overset{\textstyle S}{\textstyle \|}}{\text{SC}}\text{O}-\text{starch}$$

starch xanthide   zinc starch xanthate

starch xanthate Zn^{2+} starch xanthate
+ resorcinol $\xrightarrow{\quad or\ HNO_2 \quad}$ resorcinol-formaldehyde
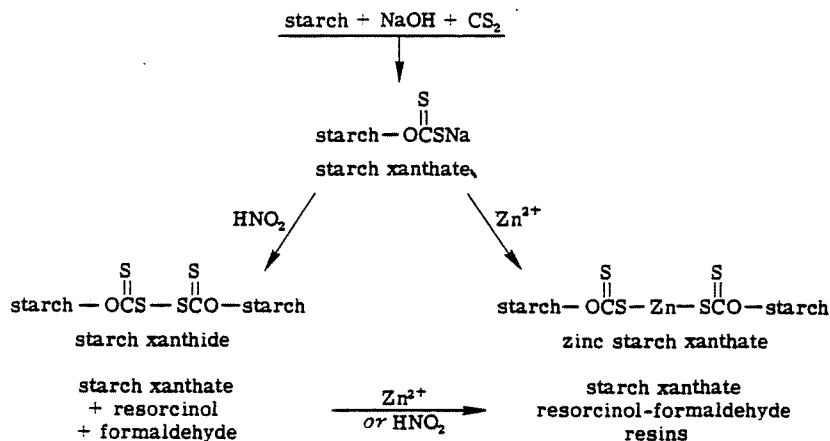+ formaldehyde   resins

FIG. 10.—Xanthation and cross-linking of starch.

open containers for several weeks, loss of even volatile pesticides was negligible. However, when products are placed in water or soil, active agent is released from the matrix.

Other polymers can be incorporated readily into the products to modify release properties. Polymers like polystyrene, polyethylene, and poly(vinyl chloride) are just dissolved in a small amount of an appropriate solvent such as benzene or acetone then added to the xanthate solution. Poly(styrene–butadiene), commercially provided as a latex, is conveniently added in this form. Upon cross-linking the xanthate, the other polymers are entrapped along with active agents.

Another modification easily made provides products which are doubly encapsulated. This is achieved on addition of more starch xanthate, either alone or containing another polymer, after the initial cross-linking reaction has been effected, and then adding additional cross-linking agent. Schreiber (56) recently reported results of greenhouse and field tests of two cross-linked starch xanthate–EPTC (S-ethyl dipropylthiocarbamate) products. One formulation con-

Table XIV

Starch–EPTC Formulations in Weed Control

	Total weed	
Treatment[a]	Count	Weight, g
Untreated	95.3	924.8
EC–EPTC	48.0	247.8
Starch–EPTC (single)	33.7	186.0
Starch–EPTC (double)	33.0	31.0

[a] Applied at a rate of EPTC of 3.36 kg/ha.

tained 14% EPTC and the other was a double-encapsulated product containing 20% latex polymer and 22% EPTC. In greenhouse and field tests, both starch formulations gave better control of weeds than the commercial formulation applied at an equivalent weight of active agent (Table XIV). The double encapsulated product gave excellent control of weeds for 120 days, whereas the commercial product controlled weeds for only about 45 days. Four companies have licensed this technology and several others are now evaluating it with their own particular pesticides. Two alternative methods to the xanthate procedure for encapsulating pesticides within a starch matrix recently have been reported. In both, the pesticide is dispersed in aqueous alkali-gelatinized starch, and the encapsulating matrix is formed by adding either calcium chloride (57) or boric acid (58).

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